An Electron Beam Method for Creating Combinatorial Libraries: Application to Next Generation Thermal Barrier Coatings Systems

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The next generation of thermal barriers coating (TBC) systems used on turbine engines must be able to endure higher operating temperatures. The thermally protective top coat layers of these TBC systems must therefore exhibit lower thermal conductivity and improved thermochemical stability. The underlying bond coat layers should have substantially improved oxidation resistance and increased high temperature strength. These properties strongly depend upon coating composition. However, as these layers become increasingly complex the relationship between composition and properties becomes difficult to predict and thus, the development of advanced materials systems is slowed. To accelerate the design and manufacture of advanced coatings we have developed a combinatorial synthesis approach. A library of compositions is created and their properties are measured using parallel measurement techniques to allow rapid investigation of a wide range of compositions. Compositionally graded libraries are directly deposited using multi-source electron beam evaporation in conjunction with an inert, transonic gas jet. The properties of the gas jet control the degree of intermixing between co-evaporated melt pools and thus, the compositional gradient of the library. Direct Simulation Monte Carlo simulations along with binary collision theory has been used to investigate the origin of the lateral compositional variation. Deposition conditions which lead to sharp, lateral composition gradients across a substrate have been identified.

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Introduction

Thermal barrier coatings (TBC) systems have been incorporated into gas turbine engines because of the high near term performance benefits that result from their use[1]. To be successful, these coatings must not only provide thermal insulation, but also must remain strongly bonded to the components surface while providing both oxidation and hot corrosion protection of the underlying component. For superalloy components, of interest in gas turbine engines, this has resulted in the design of a multilayered thermal barrier coating system consisting of a bond coat, a thermally grown oxide (TGO) film on top of the bond coat, and a low thermal conductivity top coat[2]. In most applications, the bond coat consists of a 50-150 ?m layer of either a MCrAlY (where M = Ni or NiCo) or a Pt-aluminide alloy, the TGO layer is an aluminum rich oxide, and the top coat consists of 100-500 ?m of yttria stabilized cubic zirconia (YSZ) typically with 7wt.%Y_2O_3.

Use of these multilayer systems in advanced gas turbine engines is also anticipated. However, this will require improved TBC durability and an increasing resistance to high temperature and long time exposures in corrosive environments. New materials having improved high temperature properties must therefore be developed to allow for their use in the higher temperature, corrosive environments where performance benefits are greatest. Current top coat compositions are limited by a lack of phase and thermal stability at elevated temperatures[3]. The bond coats require improved oxidation resistance and creep strength[4].

Many challenges confront the development and application of new TBC compositions. For example, a YSZ topcoat possesses a low thermal conductivity, high erosion resistance, high thermal expansion coefficient and good thermochemical stability with alumina[3,5]. This combination of properties is difficult to match with any one single material and thus, the development of novel top coat layers is a significant challenge. Initial research [6-10] indicates that many systems can potentially reduce the thermal conductivity and improve the thermal stability, however in many cases the resulting combination of properties is not superior to YSZ. Issues such as the material cost, processability and the specific thermal conductivity (i.e. the thermal conductivity scaled by the density) must also be considered.

In most cases, however, only simple systems have been explored. Increasingly complex (4 or more element systems) systems are difficult to investigate due to a general lack in understanding of the composition / property relationships and the large number of potential combinations that exist. Serial approaches often miss compositional “sweet spots” due to the time involved in evaluation. Similar issues limit the development of novel bond coat compositions. A combinatorial synthesis approach which allows high throughput screening of all compositions in a given materials system would vastly accelerate the discovery of novel compositions. For these approaches to be applied to TBCs, advanced deposition techniques are required.

Several approaches have been explored for the synthesis of combinatorial libraries. Almost all have used masks in combination with the sequential low deposition rate sputtering or molecular beam deposition of individual metals (or alloys)[11]. Subsequent

thermal homogenization is then used to creates pixels having different compositions. Such an approach is not ideal for ceramic top coat systems as complete thermal homogenization is difficult in the ceramic systems of interest and the thickness and pore morphology of the top coat (which are critical to TBC performance) are not properly recreated. In addition, samples created by these techniques also result in large, difficult to characterize libraries because the atomic fluxes do not have sharp profiles transverse to the vapor transport direction.

Many of the properties of interest are also sample size dependent. For example, the thermal conductivity of thin films is found to be as much as 50% less than that of the bulk material[12,13]. As the film thickness is extended beyond about ten microns, these size dependent effects generally disappear. Thus the creation of thick film libraries is very desirable.

Electron beam physical vapor deposition (EB-PVD) is of interest for creating thick film libraries as electron beam guns can evaporate a wide range of materials and can create high volumes of vapor when large source sizes are employed (i.e. ~ 5.0 cm diameter). The challenge for creating small, easily characterized thick film libraries is to develop a means for co-evaporating from multiple melt pools and controlling the degree of intermixing between the pools while still achieving high deposition rates. Co-evaporation from multiple pools is common in EB-PVD when multiple e-guns are employed. Jumping one e-beam across several sources[14] is, however, preferred for economic reasons. Intermixing of the sources occurs because the vapor spreads out from the source with a flux distribution described by a $\cos^n ?$ function (where n = 2,3,4 or more)[15]. These broad distributions do not result in steep composition gradients and thus, do not lend themselves to a creation of small libraries unless very small sources and unrealistically short (< 5.0 cm) source-to-substrate distances are employed.

In this work, these issues are overcome by directly deposited compositionally graded libraries using multi-source electron beam evaporation in conjunction with an inert, transonic gas jet[16,17]. Results indicate that by controlling the properties of a helium – 10 vol.% oxygen jet, the lateral spreading of an atomic flux is finely controlled and sharp lateral compositional gradients are created. The result is a small sample that contains a wide range of compositions. The jet also acts to focus the vapor onto the substrate yielding a high materials utilization efficiency and high (> 5 ?m/min.) deposition rates (even when small (3.175 mm diameter) melt pools are used). Oxide coatings with porous, columnar morphologies have been created using this approach[18]. Thus, the creation of libraries with a thickness and morphology similar to the TBC top layers currently in use is possible. The origin of the observed compositional gradients across the substrate are investigated using Direct Simulation Monte Carlo (DSMC) simulations of the gas jet properties and Binary Collision Theory (BCT).

Experimental Design

To investigate the use of multi-source evaporation and an inert gas jet for the creation of combinatorial libraries an electron beam directed vapor deposition (DVD) system was employed. In this system, high speed e-beam scanning (100 kHz) allows simultaneous

evaporation from up to four sources and thus, the composition of the vapor cloud to be altered. Differential pumping of the e-gun column permits the use of high chamber pressures (up to 66.5 Pa). This allows for the introduction of a rarefied, inert gas jet by supersonic expansion through a nozzle. The jet is created by maintaining a high pressure, P_u, upstream of the nozzle opening and a lower downstream (or chamber) pressure, P_o. The pressure ratio, P_u / P_o, the size of the nozzle opening and the specific heat of the gas determine the speed of the gas entering the chamber. The DVD system is shown schematically in Figure 1. Using this setup, 3.175 mm diameter Ni, Al and Pt source rods were co-evaporated from individual melt pools for two cases. A low chamber pressure / low pressure ratio condition and a high chamber pressure / high pressure ratio condition. The low pressure case used a chamber pressure of 8 Pa and a pressure ratio of 4.0 (case I). The higher pressure case used a chamber pressure of 27 Pa and a pressure ratio of 4.8 (case II). The composition across two directions of each coating was then measured using EDS to assess the compositional gradient across the substrate.

Results

The compositional gradients during the co-evaporation of Ni, Al and Pt were observed for the two process conditions investigated, Figures 2 and 3. When the chamber pressure and the pressure ratio were relatively low (case I), no gradients were observed across the coating. Increasing the chamber pressure and the pressure ratio (case II) led to significant gradients in the coating. Compositional measurements were made at small intervals in two orthogonal directions. Figure 3(a) shows that as the measurement is carried out in the x-direction (i.e. away from the nickel source and closer to the aluminum source) the compositions increasingly become Al-rich. Similarly, in Figure 3(b), one observes that in the positive y-direction (i.e. away from aluminum source and towards the nickel source) the compositions increasingly become nickel rich. The heaviest of the three elements (Pt), is the least influenced in spatial variations by the increased chamber pressure and pressure ratio.

Modeling Approach

A two dimensional, axisymmetric DSMC code was used to model the experimental work. The “Icarus” code used in the study was developed by Bartel and others at Sandia National Laboratories[19]. The problem geometry, boundary conditions and collision properties were set to simulate a DVD processing environment. The simulated area was divided into regions that were subsequently subdivided into cells. As required by the DSMC method, the cell size was chosen to be small enough to capture the gradients in the gas and vapor pressure, velocity, and temperature that existed in the flow field [20]. Solid surfaces were used to define the nozzle and the substrate surface. The nozzle opening for all cases was 30 mm. A 50.8 mm diameter substrate was defined 180 mm from the nozzle opening. A carrier gas flow rate was input at a point upstream of the nozzle opening. The chamber pressure was maintained at a prescribed set point. The number of particles simulated in each case was adjusted so that a minimum of twenty particles / cell were present in all cells. A time step of 1×10^{-7} seconds was used. This value was chosen so that particles did not travel further than their mean free path during a

time step. A variable hard sphere (VHS) model[20] was used to simulate binary collisions.

After the flow field was determined for both cases, a second atom tracking code using binary collision theory (BCT) was employed to simulate vapor transport. This code also utilized the VHS model to simulate collisions between the vapor atom and the background gas. Nickel atoms were input into the flowfield from a 3.175 mm diameter sources centered around one of four coordinates [(5.0 mm, 5.0 mm); (5.0,-5.0); (-5.0, 5.0); (-5.0,-5.0). The initial trajectories of the atoms were based on a $\cos^3(?)$ distribution and their initial kinetic energy was taken to be 0.39 eV[21]. For each source, 10,000 atoms were simulated. The location of each collision and the impact position of each atom on the substrate was recorded.

Simulations

The flow fields for the two gas jet conditions used in the experimental work are given in Figure 4. Note that the axial velocity component in case II remained high (> 500 m/s) for a greater distance into the chamber than case I. This resulted in a strong radial velocity component near the substrate (i.e a wall jet) and a high average jet velocity (820.32 m/sec. when measured from the nozzle to the substrate). No wall jet resulted in Case I as the jet had a relatively low average axial velocity (473.57 m/sec.). The average trajectories of the helium gas jets atoms were also different for the two cases. The trajectories in case II were approximately perpendicular to the substrate until turning parallel when they approached the substrate. In case I, the trajectories gradually expanded radially outward from the nozzle opening as they moved toward the substrate.

The effect of altering the gas jet parameters on the lateral diffusion of the vapor atoms evaporated from four sources was observed by employing the BCT code. Atom impact positions on the substrate could be plotted for both cases, Figure 5 (case I) and 6 (case II). In case I, the vapor atoms exhibited limited lateral diffusion for a distance of ~ 10 cm into the chamber. Beyond this distance the velocity of the gas jet was low (< 300 m/s) and lateral diffusion became significant as gas phase collisions now resulted in increasingly random scattering directions. Note that the positions of the atoms for the four sources would result in significant intermixing of the atoms in this case. When the chamber pressure (case II) was increased the axial jet velocity was high (> 500 m/sec.) until very close to the substrate (~ 2 cm). Lateral diffusion was limited in this high velocity region. Near the substrate, lateral diffusion occurred due to the presence of a radial jet velocity component (i.e. the wall jet), however this led to diffusion primarily away from the substrate midpoint and thus, the other co-evaporated fluxes. In this case, only limited mixing occurred and sharp composition gradients are therefore expected for this condition. This result is similar to the experimental observations above.

Discussion

The experimental and simulation results both indicate that a compositional gradient across a substrate can be observed when a high density, high velocity gas jet is used to alter vapor transport during co-evaporation of several elements. The incorporation of the

gas jet is critical as then the lateral diffusion of the vapor atoms is not determined by the $\cos^3$? distribution (as for EB-PVD) but by the frequency and nature of vapor phase collisions between the gas jet and vapor atoms. The magnitude of the gradient is dependent on the gas jet properties.

Gas jets yield a large compositional gradient when vapor atom trajectories having a small radial component a produced so that only limited lateral diffusion may occur. This is the case when conditions exist that result in the vapor atom trajectories approximately following those of the gas jet atoms. In both cases studied here, the gas jet atom trajectories extended approximately linearly from the source to substrate unless altered by a strong wall jet. The wall jet turns the trajectories parallel to the substrate, but primarily away from the other sources. Prior research[22] has indicated that vapor atoms will follow the gas jet streamlines when jet velocity is high and mean free path low (i.e. high chamber pressures). This occurs because frequent collisions with high energy gas jet atoms alter the trajectory and energy of the vapor atoms so that it approximates that of the gas jet atoms. When the velocity is low, vapor phase collisions result primarily in randomizing the vapor atom trajectories and thus enable lateral diffusion through a random walk process.

Combinatorial Libraries for TBCs

Use of a gas jet allows for the creation of steep compositional gradients that are useful for depositing combinatorial samples using a DVD approach. Platinum aluminide bond coat samples may be deposited using a similar set-up as shown above. In this case, high substrate temperatures and plasma activation may be used to create dense layers. The oxidation characteristics and strength of different pixels may then be assessed.

Top coat combinatorial libraries are created by evaporating metal sources and incorporating oxygen into the gas jet. The many binary collisions between the gas jet atoms and the vapor atoms result in the formation of metal oxide molecules which then deposit on the substrate. This approach allows the use of easily evaporated metal source rods and facilitates the deposition of a wide variety of elements. The morphology of coatings created this way has been observed to be similar to the columnar coatings used in service[18], thus when thick layers are deposited the thermal conductivity can be measured and the thermal stability can be assessed.

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Figure Captions

Figure 1 – Electron beam directed vapor deposition (EB-DVD). A high scan frequency (100KHz) electron beam is used to simultaneously evaporate up to four source materials (two shown). The lateral spread of evaporant from each source is controlled by the velocity and pressure of annular helium gas jets.

Figure 2 - SEM/EDS measured composition variation with substrate position in two orthogonal directions when using a chamber pressure of 8 Pa and a pressure ratio of 4.0.

Figure 3 - SEM/EDS measured composition variation with substrate position in two orthogonal directions when using chamber pressure of 27 Pa and a pressure ratio of 4.8.

Figure 4 –DSMC simulations showing the velocity profile of a helium gas jet during a supersonic expansion. In a) and b) the axial jet velocity component is plotted for case I and II respectively. In c) and d) the radial jet velocity component is given.

Figure 5 – Plots showing the impact positions of atoms leaving from one of four sources (a – d) when using the process conditions of Case I. Significant intermixing between the sources results.

Figure 6 – Plots showing the impact positions of atoms leaving from one of four sources (a – d) when using the process conditions of Case II. Very little intermixing between the sources results.

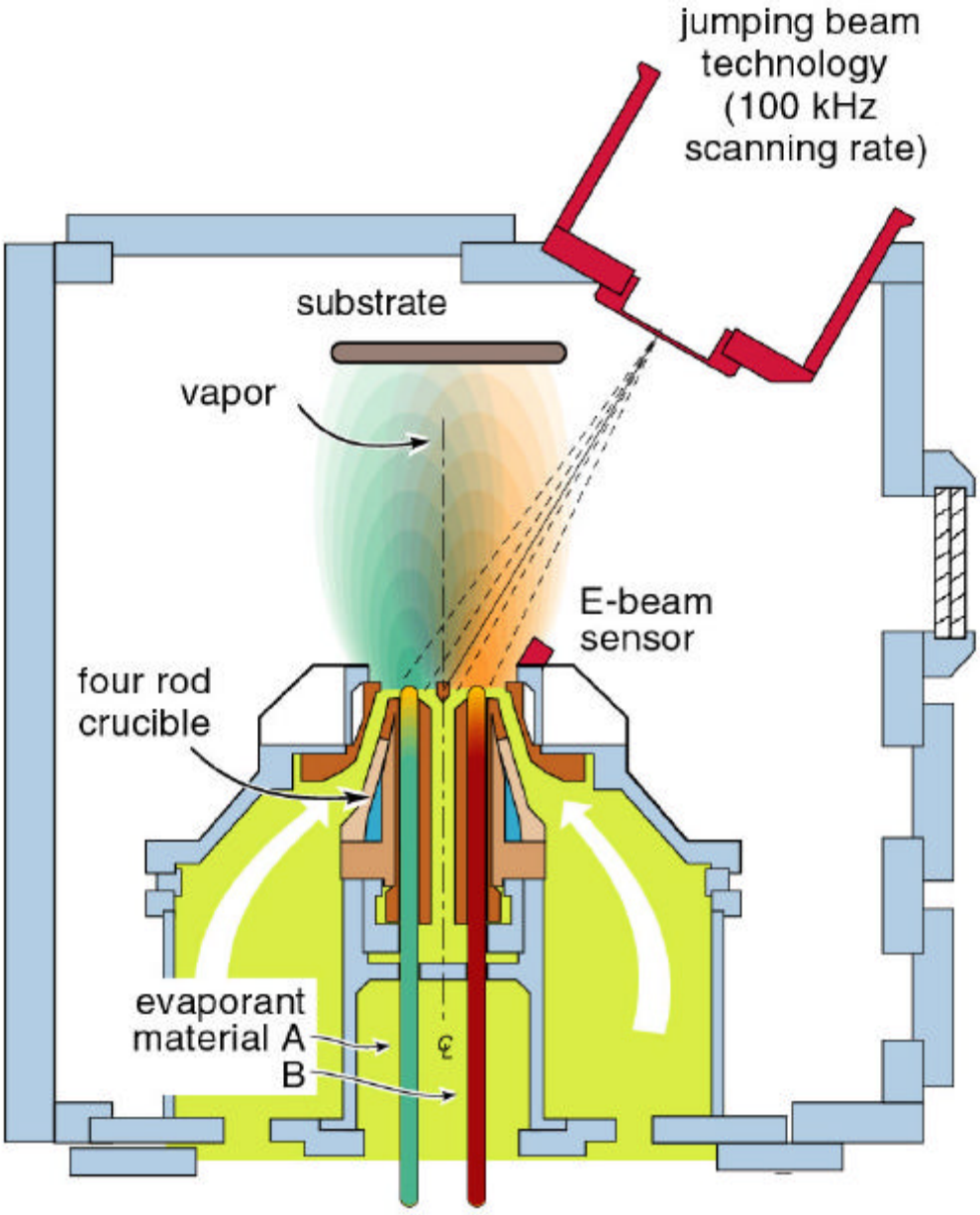
jumping beam
technology
(100 kHz
scanning rate)
substrate
vapor
E-beam
sensor
four rod
crucible
evaporant
material A
B

Figure 1

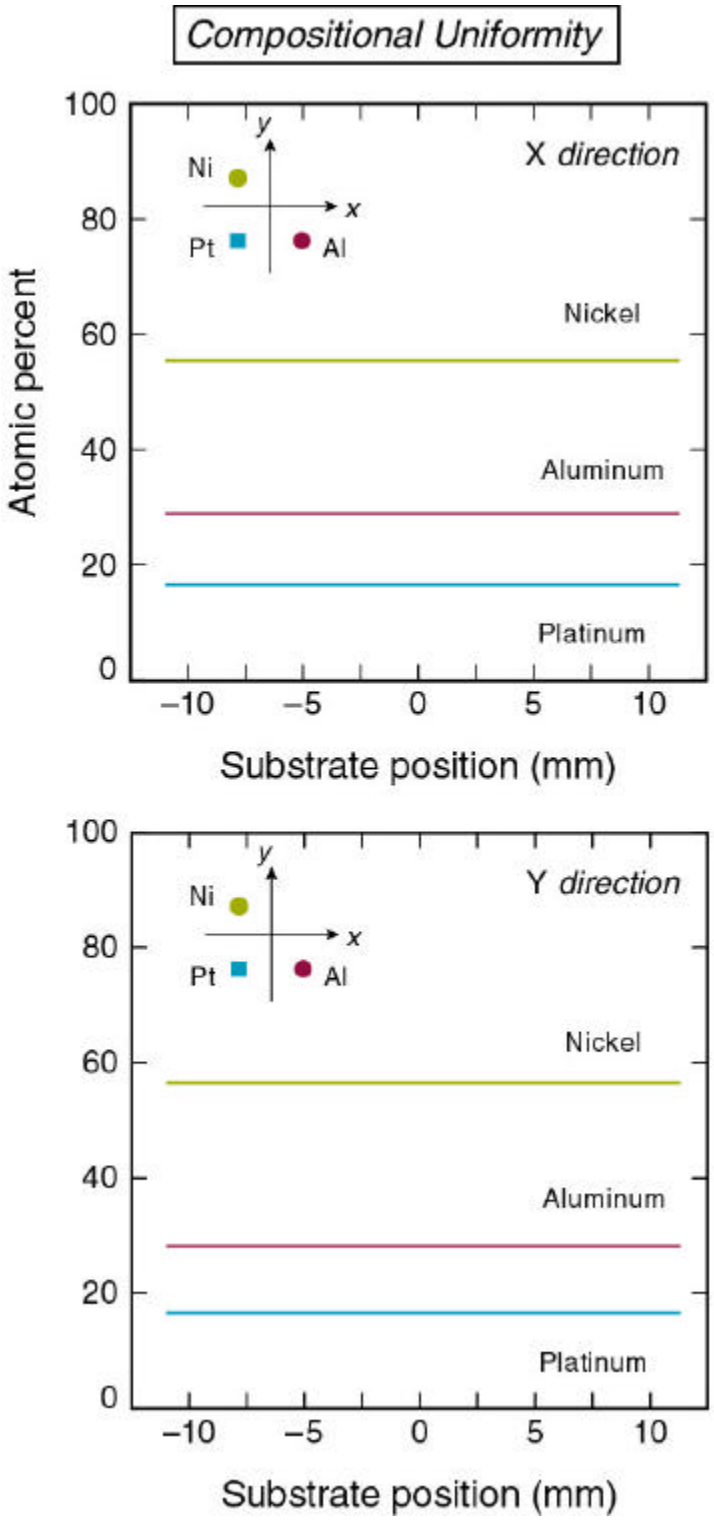
Compositional Uniformity
X direction
Y direction
Ni
Pt
Al
y
x
Nickel
Aluminum
Platinum
Atomic percent
Substrate position (mm)
100
80
60
40
20
0
−10
−5
0
5
10

Figure 2

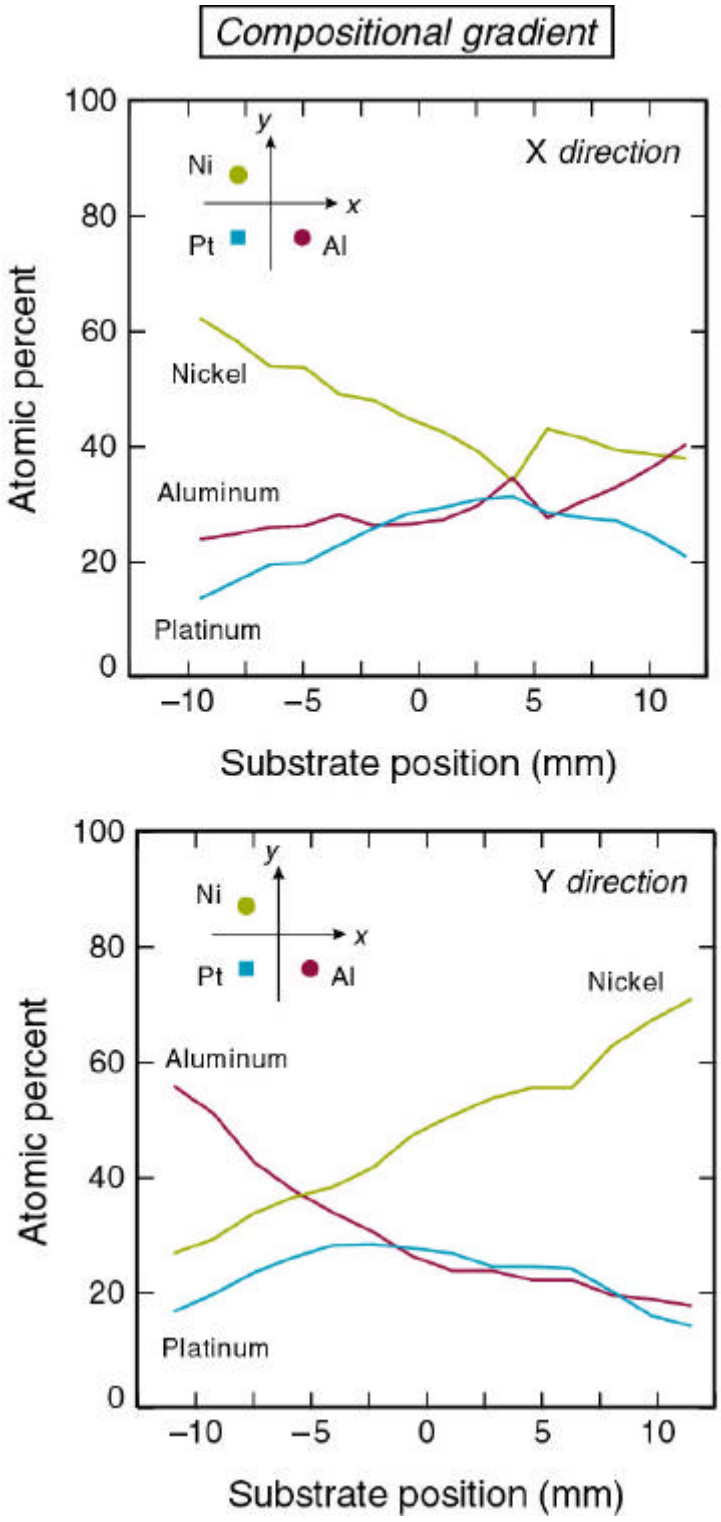
Compositional gradient
X direction
Y direction
Ni
Pt
Al
x
y
Nickel
Aluminum
Platinum
Atomic percent
Substrate position (mm)
100
80
60
40
20
0
−10
−5
0
5
10

Figure 3 -

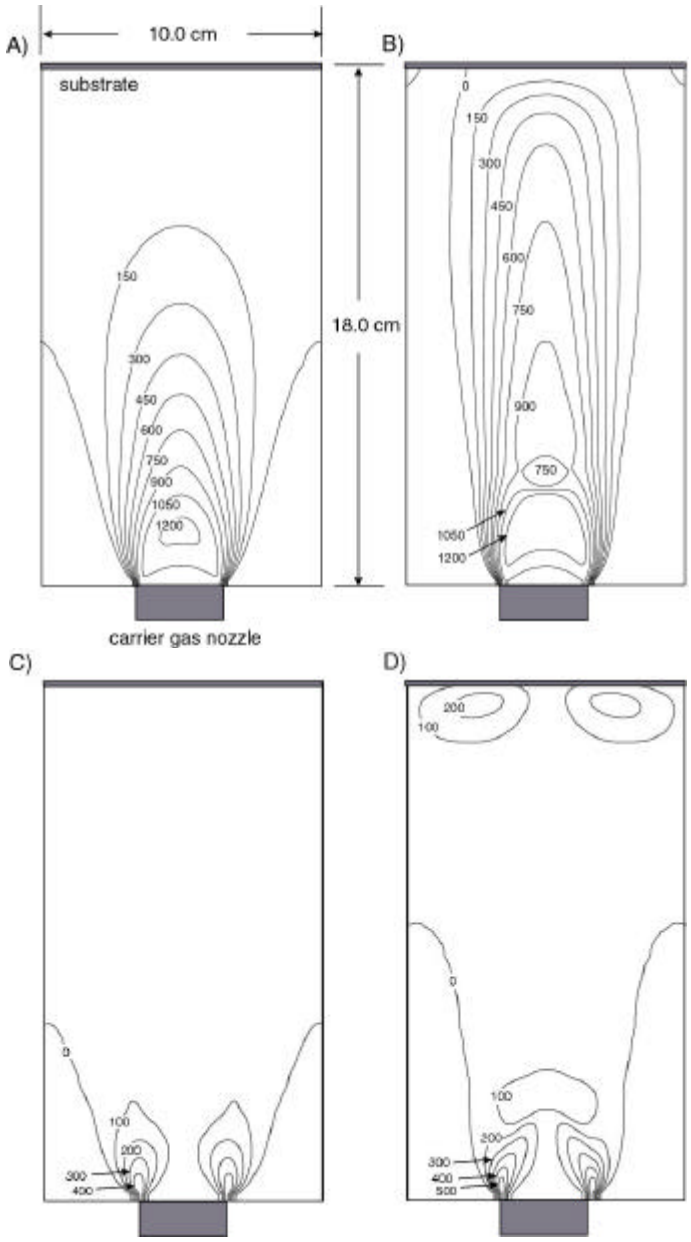
A)
10.0 cm
substrate
150
300
450
600
750
900
1050
1200
18.0 cm
carrier gas nozzle
B)
0
150
300
450
600
750
900
750
1050
1200
C)
0
100
200
300
400
D)
200
100
0
100
300
300
400
500

Figure 4 -

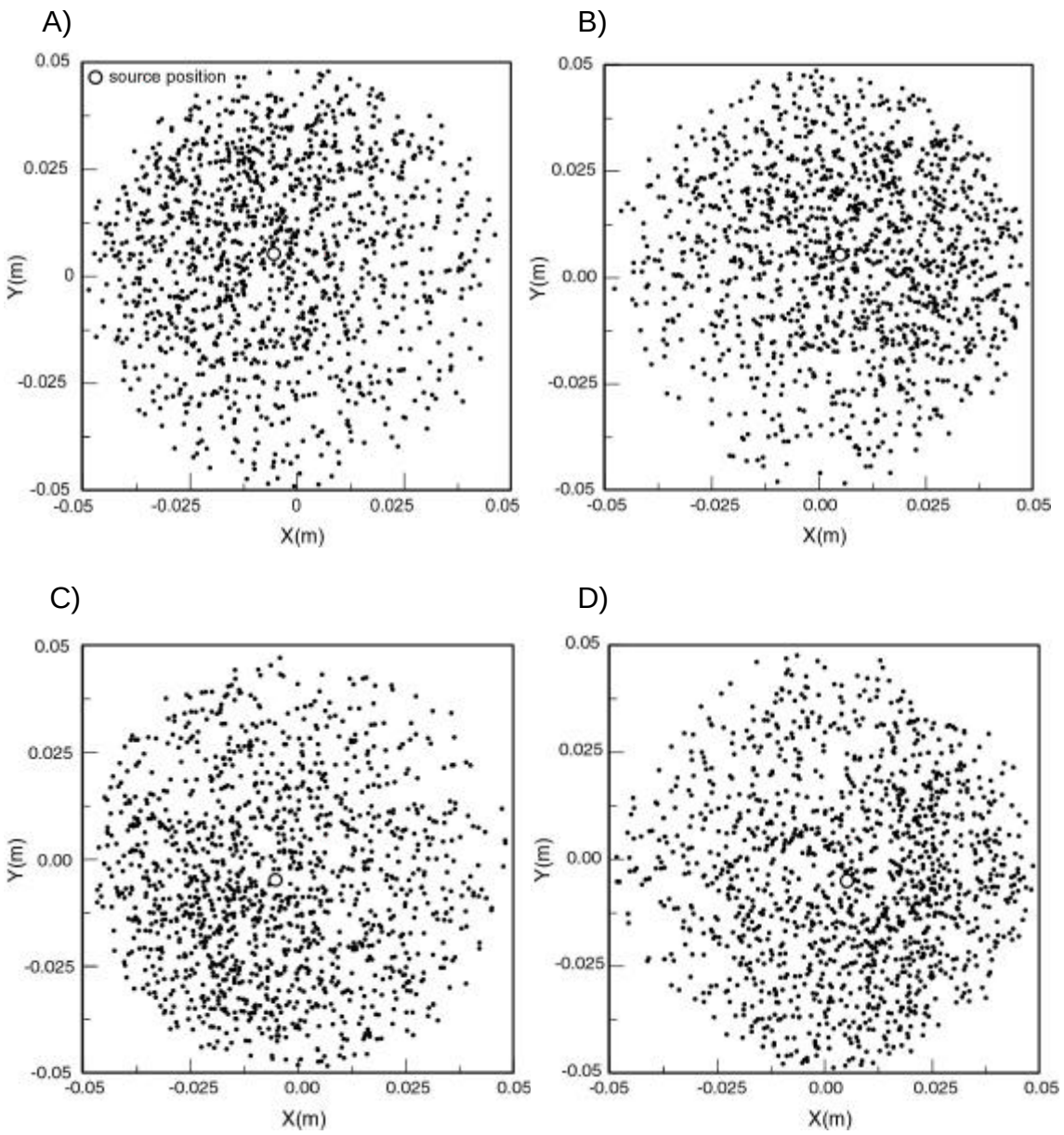

Figure 5 –

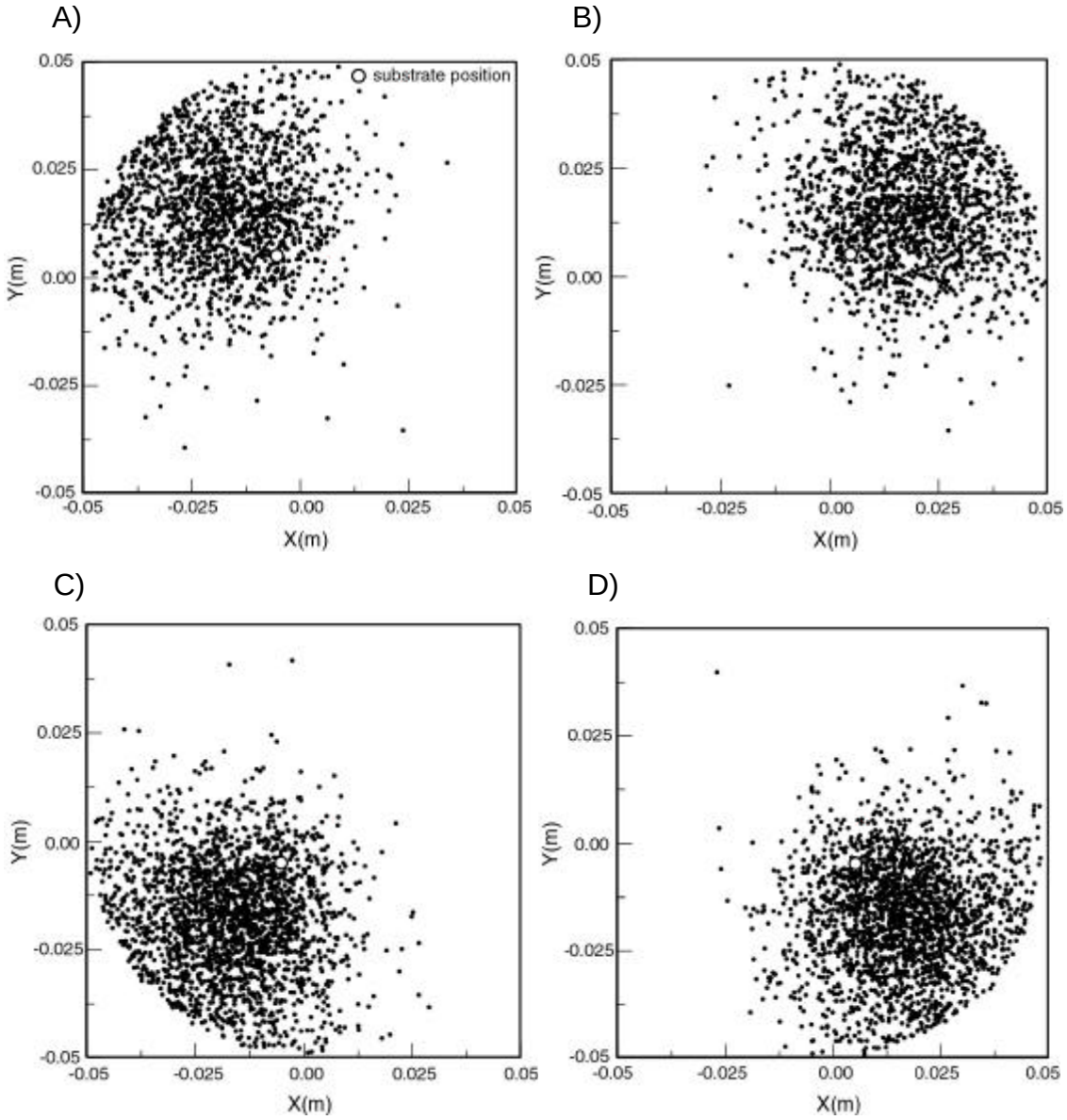

Figure 6 –